EUROPEAN PATENT OFFICE

Patent Abstracts of Japan

PUBLICATION NUMBER : 57116799
PUBLICATION DATE : 20-07-82

APPLICATION DATE : 09-01-81
APPLICATION NUMBER : 56002264

APPLICANT : KOBE STEEL LTD;

INVENTOR : URAI MASAAKI;

INT.CL. : C25D 5/36 // C25D 3/38

TITLE : METHOD FOR COPPER PLATING

ABSTRACT : PURPOSE: To obtain a copper plating layer of good adhesive strength by electrolytically pickling a steel material in an aq. sulfuric acid which contg. thiourea or its deriv. without using cyanide harmful for sanitation then electroplating the same in a copper sulfate bath.

CONSTITUTION: About 0.005~0.5g/lthiourea or deriv. of thiourea such as aryl thiourea is added into an aq. sulfuric acid contg. about 20~100g/l sulfuric acid, and with a steel material as cathode, an electrolytic pickling treatment is accomplished at about 10~40°C, about 10~500A/dm^2 current density and for about 0.5~10sec electricity conduction time. Immediately after this without washing by water, the steel material is electroplated with a copper sulfate plating bath similar to that by known methods. The thiourea or its deriv. electrostatically charges to ⊕ in the pickling bath, sticks and coats the surface of the steel material electrically in the electrolytic pickling stage, prevents replacement plating reaction in the electroplating stage and improves the adhesive strength of the copper plating layer considerably.

⑲ 日本国特許庁（JP）　　⑪ 特許出願公開

⑫ 公開特許公報（A）　　昭57—116799

⑤1Int. Cl.³	識別記号	庁内整理番号	④3公開　昭和57年(1982)7月20日
C 25 D 5/36		6575—4K	
//C 25 D 3/38	101	6575—4K	発明の数　1
			審査請求　未請求

（全 5 頁）

⑤4銅めつき方法

②1特　　願　昭56—2264
②2出　　願　昭56(1981)1月9日
⑦2発 明 者　福塚敏夫
神戸市東灘区御影山手6—5—6
⑦2発 明 者　下郡一利
神戸市垂水区西舞子8丁目4—35
⑦2発 明 者　浦井正章
加古川市志方町上富木86—10
⑦1出 願 人　株式会社神戸製鋼所
神戸市中央区脇浜町1丁目3番18号
⑦4代 理 人　弁理士　植木久一

明　細　書

1.発明の名称

銅めつき方法

2.特許請求の範囲

(1)鋼素地上へ銅めつき層を形成するに当り、チオ尿素又はその誘導体を含有する硫酸水溶液中で、被めつき鋼材を陰極として電解酸洗を行なつた後、硫酸銅浴中で電気めつきを行なうことを特徴とする銅めつき方法。

3.発明の詳細な説明

本発明は銅めつき方法に関し、殊に硫酸銅浴を用いて鋼素地の表面に密着性の良好な銅めつき層を形成する方法の改良に関するものである。

従来、硫酸銅浴を用いて密着性の良好な銅めつき層を形成する為には、硫酸銅電気めつきに先立つてシアン化銅浴によるストライクめつきを行なうことが不可欠とされていた。しかしながらこの工程は、シアン化物を含有する排液公害を生じるという重大な問題があり、かかる問題を回避する為にはシアン化合物を用いない銅めつき法の確立が必要で、多くの研究が行なわれている。

これら改良研究の殆んどは、硫酸銅浴中での電気めつき工程で起こる鉄と鋼との置換めつき反応を抑制し、銅めつき層の密着性低下を防止しようとするものである。例えば特公昭37-5708号には、酸蝕抑制剤を含む酸洗浴で被めつき材を予備処理した後硫酸銅浴中で電気めつきを行なうことにより、密着性の良い銅めつき層が得られると報告されている。また特公昭54-4829号は、硫酸銅浴に置換抑制剤としてアリル-チオ尿素を添加し、置換めつき反応を抑制しつつ電気めつきを行なうことによつて、銅めつき層の密着性を高めようとするものである。

本発明者等もかねてよりシアン化合物を使用しない銅めつき法の開発を期して種々研究を行なつているが、その研究の過程で前記公告公報記載の方法を追試した。その結果、銅めつき層の密着性に関しては、記載された程の効果が得られなかつた。そこでその理由を追求したところ、以下に示す様な事実が確認された。即ち上記公報記載の方

法は、被めつき材の表面全域を酸蝕抑制剤又は置換抑制剤で被覆することによつて置換めつき反応を抑制しようとするものであるが、ミクロ的見地からすると被覆効果が不十分であつて置換めつき反応を完全に防止することができず、部分的には置換めつき反応が起こつて当該部分の密着性が低下する。従つて電気めつき工程に先立つて、これらの薬剤で被めつき材表面全域を完全に被覆することができ、且つ電気めつきを阻害しない様な予備処理法を確立してやれば、電気めつき層の密着性を高めることができると考えた。

本発明はかかる知見を基に、予備処理法の改善によつて電気銅めつき層の密着性を高めるべく鋭意研究の結果完成されたものであつて、その構成は、鋼素地上へ銅めつき層を形成するに当り、チオ尿素又はその誘導体を含有する硫酸水溶液中で、被めつき鋼材を陰極として電解酸洗を行なつた後、硫酸銅浴中で電気めつきを行なうところに要旨が存在する。

本発明では、酸洗用の硫酸水溶液中にチオ尿素

又はその誘導体を添加しておき、被めつき材を陰極として電解酸洗を行なうが、チオ尿素やその誘導体は硫酸水溶液中で⊕に帯電しているから、電解酸洗工程では浄化された被めつき材の表面に電気的に引き寄せられ、被めつき材の表面全域を完全に被覆する。従つてこの予備処理の後硫酸銅浴に導いて電気めつきを行なうと、全面電気めつきからなる密着性の優れた銅めつき層を得ることができる。この場合、予備処理後は水洗することなくそのまま電気めつきを行なうのがよい。尚前記公告公報記載の方法においても、酸蝕抑制剤又は置換抑制剤としてチオ尿素やその誘導体を使用できる旨記載されている。しかしこれらの方法では、上記の薬剤を酸洗浴又は置換銅めつき浴等に添加して置換めつき反応を抑制しようとするものであり、これらの薬剤の被めつき材表面への付着は物理的な付着のみであるから、チオ尿素等を多量添加して被覆剤濃度を高める必要があると共に、仮に濃度を十分に高めた場合でも、ミクロ的見地からみると完全な被覆効果は得られない。また電解

めつき浴中にチオ尿素等を添加し、電解めつき工程で同時にチオ尿素等による表面被覆効果を発揮させて置換めつきを抑制する方法も考えられる。しかしこの方法では、電気めつきの初期段階で置換めつき反応が併発し、密着性はやはり不十分になる。これらに対し本発明の方法では、銅イオンの全く存在しない酸洗処理の段階で、被めつき材の表面全域にチオ尿素等を電気的に付着させて被覆する方法であるから、比較的低濃度のチオ尿素等であつても十分な効果を得ることができ、被覆効果も殆んど完全無欠である。更に上記公告公報記載技術の改善法として、アセチルチオ尿素を含む酸洗浴に被めつき材を浸漬して酸洗した後、アセチルチオ尿素を含む硫酸銅浴で置換めつきを行ない、水洗後硫酸銅浴中で電気めつきを行なう方法が報告されている。しかしこの方法は予備処理が煩雑であると共に、置換めつき工程での浴組成が僅かに違うだけで密着性が極端に低下する傾向があり、しかもアセチルチオ尿素の付着は前記と同様所詮物理付着のみであるから、置換めつき反

応抑制効果は本発明法に比べてはるかに劣る。

本発明で使用するチオ尿素又はその誘導体は、前述の如く酸洗浴中で⊕に帯電し、電解酸洗工程で電気的に被めつき材表面に付着して表面被覆効果を発揮するもので、チオ尿素誘導体としては、アリルチオ尿素、アセチルチオ尿素、N－アリル－N′－アルキルチオ尿素、N－アルアルキル－N′－アルキルチオ尿素、N－シクロアルキル－N′－アルキルチオ尿素、N－アルキル－N′－アルキルチオ尿素、β－アルキルチオ尿素及びそのN－アルキル置換体、N－フエニル－N′－オキシエチルチオ尿素、N－シクロヘキシル－N′－オキシエチルチオ尿素、N－アルキル－N′－オキシエチルチオ尿素、N－フエニル－N′－オキシプロピルチオ尿素、N－フエニル－N′－β－（オキシエトキシ）－エチルチオ尿素、N－ベンジル－N′－オキシエチルチオ尿素、N－4－オキシフエニル－N′－オキシエチルチオ尿素等が例示される。上記誘導体中のアルキル残基としては、炭素数が6以下の低級アルキル基が好ましい。これらの中でも最も優

れた効果を発揮するのはチオ尿素、アリルチオ尿素及びアセチルーチオ尿素である。尚後記実験例でも明らかにする如く、チオ尿素等と同様酸洗浴中で⊕に帯電するアミン系化合物を使用しても電解めつき層の密着性は全く改善されず、本発明者等が実験した限り前述の様な優れた密着性向上効果を発揮するのはチオ尿素及びその誘導体のみであつた。

電解酸洗浴として使用する硫酸水溶液の濃度は特に限定されないが、最も好ましいのはその1ℓ中に硫酸20～100gを含有するものであり、チオ尿素又はその誘導体はこの水溶液中に0.005～0.5g／ℓ、より好ましくは0.01～0.2g/ℓ添加される。電解酸洗処理は、上記酸洗浴（好ましくは10～40℃程度）中で、鋼素地を陰極として通電することによつて行なわれるが、このときの最も好ましい電流密度は10～500A/dm^2、通電時間は0.5～10秒程度である。尚鋼素地は予め脱脂しておくのがよい。この様にして電解酸洗を行なうと、鋼素地の表面全域にチオ尿素又は

その誘導体が付着するから、その後硫酸銅めつき浴に導いて電気めつきを行なえばよい。電気めつき処理は公知の方法と全く同様にして行なえばよく、例えば水1ℓ当り硫酸銅170～850gを含有する硫酸銅めつき浴を用い、温度10～80℃、電流密度5～800A/dm^{2}で通電することによつて行なわれる。この場合硫酸銅めつき浴にも少量のチオ尿素又はその誘導体を添加することができる。

本発明は概略以上の様に構成されており、チオ尿素又はその誘導体を含む酸洗浴を用いた電解酸洗法を採用することによつて、電気めつき工程での置換めつき反応を防止し銅めつき層の密着性を大幅に高め得ることになつた。しかも本発明では、鋼素地の酸洗工程で同時に置換めつき防止用予備処理を行なうものであるから、予備処理工数が増加したり処理時間が延長する等の問題もなく極めて実用に即した方法と言える。

次に実験例を示す。

実験例1

濃硫酸を609g／ℓ含有する硫酸水溶液に0.1g／ℓのチオ尿素を加えて電解酸洗液を調製し、この浴に脱脂処理した鋼線材を浸漬走行させながら、電流密度800A/dm^{2}で1秒間の電解酸洗を行なう。この予備処理線材を水洗することなく硫酸銅めつき浴（$CuSO_4 \cdot 5H_2O$：80g／ℓ、濃H_2SO_4：40g／ℓ）に導き、電流密度200A／dm^2、線材走行速度：250m／分で2秒間電気めつきを行ない、得られた銅めつき鋼線材の密着性及びめつき液中への鉄の溶出量を調べた。尚密着性は、得られた銅めつき鋼線10本を共巻き試験に付し、銅めつき層に全く剥離が認められないものの数で判断した。

また電解酸洗液にチオ尿素を添加しなかつた他は上記と同様にして電解酸洗及び電気めつきを行ない、密着性及び鉄溶出量（被めつき材の単位表面積当りの溶出量）を調べた。

結果を第1表に示す。

（以下余白）

第　1　表

チオ尿素添加の有無	密着性	鉄溶出量（g／m^2）	備考
有	10／10	0.5	実施例
無	6／10	1.7	比較例

第1表からも明らかな様に、本発明法（実施例）ではめつき液への鉄溶出量が極めて少なく密着不良のものは皆無であるが、チオ尿素の添加を省略した比較例ではめつき液への鉄溶出量が多く置換めつき反応が起こつており、4割もの密着不良品が発生している。

実験例2

実験例1の方法に準じて、置換めつき防止剤の種類を変えて電解酸洗及び電気めつきを行ない、銅めつきの密着性及び電気めつき液への鉄溶出量を調べた。また参考の為、置換めつき防止剤を電気めつき浴へ添加した場合の効果も調べた。

結果を第2表に一括して示す。

第　2　表

置換めつき防止剤			密着性	鉄溶出量 (g/m²)	備考
添加場所	種　類	添加量			
電解酸洗液	チオ尿素	0.1g/ℓ	10/10	0.5	実施例
	アリルチオ尿素	0.1g/ℓ	10/10	0.8	
	アセチルチオ尿素	0.1g/ℓ	10/10	0.4	
	アミンA	1cc/ℓ	0/10	1.1	比較例
	アミンB	1cc/ℓ	0/10	1.1	
	アミンC	1cc/ℓ	0/10	1.0	
電気めつき液	チオ尿素	0.1g/ℓ	7/10	0.7	参考例
	アリルチオ尿素	0.1g/ℓ	7/10	0.6	
	アセチルチオ尿素	0.1g/ℓ	7/10	1.0	
	アミンA	1cc/ℓ	0/10	1.4	
	アミンB	1cc/ℓ	0/10	1.8	
	アミンC	1cc/ℓ	0/10	1.8	
無　添　加			6/10	1.7	

アミンA：イビットNo.8－600（住友化学社製商品名）
アミンB：イビットNo.600－LA（住友化学社製商品名）
アミンC：イビットNo.580（住友化学社製商品名）

(11)

実験例4

酸洗液中に0.1g/ℓのチオ尿素を添加し、通電することなく単なる浸漬酸洗法を採用した他は実験例1と同様にして鋼めつきを行なつた。得られた鋼めつき鋼線材の密着性は8/10であり、約2割の確率で密着不良品を発生することが分る。

即ち相当量のチオ尿素を酸洗液に添加した場合であつても、電解酸洗法を採用しない限り本発明の目的は達成できない。

4.図面の簡単な説明

第1～3図は、チオ尿素、アリルーチオ尿素及びアセチルーチオ尿素の添加量と密着性の関係を示すグラフである。

出願人　株式会社神戸製鋼所
代理人　弁理士　植木久一

(13)

第2表からも明らかな様に、アミン化合物は電解酸洗液中で⊕に帯電していると考えられるが、その密着性改善効果は全く認められず、無添加のものよりもはるかに悪い。またチオ尿素等は電解酸洗液に添加したときに限つて卓越した密着性改善効果を発揮しており、電気めつき液のみに添加しても十分な効果は得られない。

実験例3

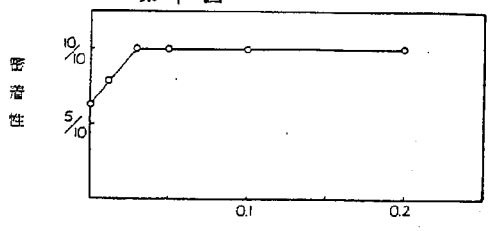
置換めつき防止剤としてチオ尿素、アリルチオ尿素及びアセチルチオ尿素を選択し、実験例1の方法に準じて夫々の添加量と密着性の関係を調べた。

結果を第1図（チオ尿素）、第2図〔アリルチオ尿素）及び第3図（アセチルチオ尿素）に夫々示す。

第1～3図からも明らかな様に、十分な密着性を確保する為には、チオ尿素で0.08g/ℓ以上、アリルチオ尿素で0.01g/ℓ以上、アセチルチオ尿素で0.02g/ℓ以上を夫々電解酸洗液中に添加することが望まれる。

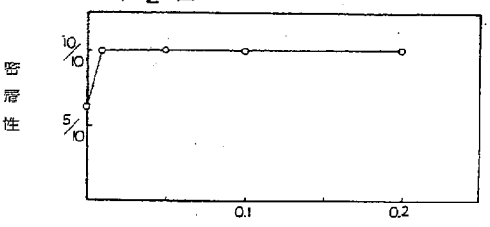
(12)

第 1 図



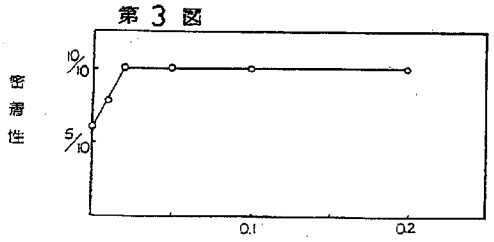
チオ尿素の添加量（g／ℓ）

第 2 図



アリルーチオ尿素の添加量（g／ℓ）

第 3 図



アセチルーチオ尿素の添加量（g／ℓ）

(19) Japan Patent Office (JP)
(11) Publication Number of Patent Application
No. S57-116799
(12) Publication of Patent Application
(43) Date of Publication of Application: July 20, 1982
(51) Int. Cl.^{3}
C 25 D 5/36
C 25 D 3/38
Identification Number
101
Intraoffice Reference Number
6575-4K
6575-4K
Number of Claims: 1
Request for Examination: not filed
(5 pages in total)

(54) Title of the Invention: COPPER PLATING METHOD

(21) Application Number: S56-2264
(22) Application Date: January 9, 1981

(72) Inventor: Toshio FUKUTSUKA
6-5-6, Yamate, Mikage, Higashinada-ku, Kobe-shi
(72) Inventor: Kazutoshi SHIMOGORI
8-4-35, Nishimaiko, Tarumi-ku, Kobe-shi
(72) Inventor: Masaaki URAI
86-10, Kamitomiki, Shikata-cho, Kakogawa-shi
(71) Applicant: KOBE STEEL LTD.
1-3-18, Wakihama-cho, Chuo-ku, Kobe-shi
(74) Agent: Patent Attorney, Kazuhisa UEKI

SPECIFICATION

1. TITLE OF THE INVENTION

COPPER PLATING METHOD

2. CLAIMS

A copper plating method for forming a copper plating layer on a steel base material, comprising

a first step of electrolytic pickling a steel material to be plated in a sulfuric acid aqueous solution containing thiourea or a thiourea derivative, the steel material being the cathode, and

a second step of electroplating the steel material in a copper sulfate bath.

3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a copper plating method, especially an improved version of a method for forming a copper plating layer with excellent adhesive property on the surface of a steel base material by using a copper sulfate bath.

Conventionally, in order to form a copper plating layer with excellent adhesive property by using a copper sulfate bath, it has been indispensable to perform strike-plating in a copper cyanide bath prior to the copper sulfate electroplating. This process, however, problematically causes pollution due to the waste liquid containing cyanides. It has therefore been desired to establish a copper plating method in which a cyanide is not used, and many researches have been conducted to achieve this goal.

Most of those researches aim to suppress displacement plating reaction between the copper and the steel that occurs in the electroplating process in the copper sulfate bath so as to prevent deterioration of the adhesive property of the copper plating layer. For example, JP-B S37-5708 has reported that a copper plating layer with excellent adhesive property can be obtained by preliminary processing a material to be plated in a pickling bath containing an pickling inhibitor and then electroplating the material in a copper sulfate bath. Moreover, JP-B 54-4329 discloses an invention aiming to improve the adhesive property of a copper plating layer by adding

allylthiourea as displacement inhibitor in a copper sulfate bath so as to suppress displacement plating reaction and then performing electroplating.

The present inventors have conducted various researches to develop a copper plating method in which a cyanide is not used. During the researches, the present inventors conducted supplemental examinations of the methods disclosed in the foregoing patent publications. As a result, it was found that the effects on the adhesive property of the copper plating layer were not as much as those disclosed in the documents. The present inventors pursued the reasons and found the following. Namely, according to the methods of the above patent publications, the displacement plating reaction is inhibited by coating the whole surface of the material to be plated with a pickling inhibitor or a displacement inhibitor. From a microscopic point of view, however, the effect of the coating is insufficient for fully inhibiting the displacement plating reaction. Therefore, the displacement plating reaction occurs in some parts so that the adhesive property of the parts deteriorates. Based on the findings, the present inventors assumed that it was possible to improve the adhesive property of the electroplating layer by establishing a preliminary processing method in which the whole surface of a material to be plated can be fully coated with the foregoing agents, and accordingly the electroplating may not be inhibited.

The present invention has been devised as a result of the intensive investigations to increase the adhesive property of the electroplating layer by improving the preliminary processing method based on the foregoing findings. The gist of the present invention is to firstly carry out electrolytic pickling of steel material to be plated in a sulfuric acid aqueous solution containing thiourea or a thiourea derivative, the steel material being the cathode, and then electroplating the steel material in a copper sulfate bath, in the process of forming a copper plating layer on the steel base material.

According to the present invention, thiourea or a thiourea derivative is added to an aqueous sulfuric acid solution for pickling, and electrolytic pickling of the material to be plated is performed with the material as the cathode. In this process, as the thiourea or the thiourea derivative is positively charged in the aqueous sulfuric acid solution, the thiourea or the thiourea derivative is electrically drawn to the surface of the material to be plated which has been washed in the electrolytic pickling process so as to fully coat the whole surface of the material to be plated. Accordingly, when the resulting material to be plated after the preliminary processing is subjected to electroplating in a copper sulfate bath, the whole surface of the material can be electroplated with a copper layer with excellent adhesive property. In this process, it is preferable to perform the electroplating without water-washing after the preliminary processing. Meanwhile, use of thiourea or a thiourea derivative as a pickling inhibitor or a displacement inhibitor is described in the methods of the aforementioned patent publications. However, according to those methods, the inhibitor is added to the pickling bath or the displacement copper plating bath so as to inhibit displacement plating reaction. Thus, as the adhesion of the agent to the material to be plated is based only on physical adhesion, it is necessary to increase the concentration of the coating agent by adding a large amount of thiourea or similar agents. Furthermore, even if the concentration is sufficiently increased, a perfect coating effect cannot be obtained from a microscopic point of view. It may be possible to exemplify another method for inhibiting displacement plating, in which thiourea or a similar agent is added to an electroplating bath so that the surface coating effect of the thiourea or the similar agent is achieved in the electroplating bath. In this method, however, a displacement plating reaction concomitantly occurs at an early stage of the electroplating, resulting in insufficient adhesive

property. On the other hand, according to the method of the present invention, the whole surface of the material to be plated is electrically coated with thiourea or a similar agent at a stage of the pickling process where no copper ions exist. For this reason, it is possible to achieve sufficient effects even with the thiourea or the similar agent having a relatively low concentration, and furthermore, the resulting coating effect is almost perfect. Furthermore, in order to improve the techniques described in the aforementioned patent publications, it has been reported a method in which: a material to be plated is immersed in a pickling bath containing acetylthiourea for electrolytic pickling; the material to be plated is then subjected to displacement plating in a copper sulfate bath containing acetylthiourea; water-washing is performed; and the resulting material is electroplated in a copper sulfate bath. This method, however, has problems; namely, the preliminary processing is complicated, and even a slight change in the composition of the bath tends to extremely decrease the adhesive property of the resulting product. Additionally, since the acetylthiourea is only physically adhered similarly as the above case, the effects of inhibiting displacement plating reaction is far inferior to the method according to the present invention.

The thiourea or a thiourea derivative used in the present invention is positively charged in the pickling bath as mentioned earlier and is electrically adhered to the surface of the material to be plated to exert the surface coating effect. Examples of the thiourea derivative include allylthiourea, acetylthiourea, N-ally-N'-alkylthiourea, N-aralkyl-N'-alkylthiourea, N-cycloalkyl-N'-alkylthiourea, N-alkyl-N'-alkylthiourea, 8-alkylthiourea and N-alkyl substituted analogs thereof, N-phenyl-N'-oxyethylthiourea, N-cyclohexyl-N'-oxyethylthiourea,
N-phenyl-N'-oxypropylthiourea,
N-phenyl-N'-β-(oxyethoxy)-ethylthiourea,

N-benzyl-N-oxyethylthiourea, and N-4-oxyphenyl-N'-oxyethylthiourea. Examples of the alkyl residue in the derivative preferably include lower alkyl groups having 6 or less carbons. The examples showing the most excellent effects among the above examples are thiourea, allylthiourea, and acetyl-thiourea. As will be clearly shown by Examples mentioned below, in the case where an amine compound, which is positively charged in the pickling bath similarly as thiourea, is used, the adhesive property of the resulting electroplating layer is not at all improved. Based on the examination results conducted by the present inventors or others, it is only thiourea or a thiourea derivative that can exert excellent adhesive property-improving effects as mentioned earlier.

The concentration of the aqueous sulfuric acid solution to be used as an electrolytic pickling bath is not particularly limited. The most preferable example is an aqueous sulfuric acid solution containing 20 to 100 g of sulfuric acid in one liter of the solution, in which thiourea or a thiourea derivative is contained in an amount of 0.005 to 0.5 g/l, or preferably 0.01 to 0.2 g/l. The electrolytic pickling is performed by supplying electricity to the steel base material as the cathode in the aforementioned pickling bath (preferably at a temperature of 10 to 40°C). In this process, the electric current density is preferably 10 to 500 A/dm^2 and the electricity supplying time is preferably about 0.5 to 10 seconds. The steel base material is preferably degreased in advance. When the electrolytic pickling is performed in the aforementioned manner, the thiourea or the thiourea derivative is adhered to the whole surface of the steel base material. Thereafter, the material may be introduced to a copper sulfate plating bath for electroplating. The electroplating may be performed in the same manner as conventional methods, for example, by using a copper sulfate plating bath containing 170 to 850 g of copper sulfate per one liter of water and supplying electricity at a

temperature of 10 to 80°C and with the current density of 5 to 300 A/dm^2. It is possible to add a small amount of the thiourea or the thiourea derivative in the copper sulfate plating bath.

The present invention with the above-outlined structure can greatly improve the adhesive property of the copper plating layer by employing the electrolytic pickling method in which the pickling bath contains thiourea or a thiourea derivative and thus displacement plating reaction can be prevented from occurring in the electroplating process. Moreover, according to the present invention, the preliminary processing for preventing displacement plating is simultaneously performed during pickling of the copper base material, and thus problems such as increase of the number of preliminary processing and a longer processing time do not occur. Therefore, the present invention is extremely useful and practical.

Examples of the present invention are described below.

Example 1

An electrolytic pickling solution was prepared by adding 0.1 g/l of thiourea in an aqueous sulfuric acid solution containing 60 g/l of concentrated sulfuric acid. By immersing and running a degreased steel wire in the thus obtained electrolytic pickling bath, the wire was electrolytic pickled with the current density of 800 A/dm^2 for one second. The preliminary processed steel wire was introduced into a copper sulfate plating bath ($CuSO_4 \cdot 5H_2O$: 300 g/l, concentrated H_2SO_4: 40 g/l) without water washing, and subjected to electroplating for two seconds (current density: 200 A/dm^2, running speed of steel wires: 250 m/min.). The resulting copper-plated steel wire was examined for the adhesive property and the amount of iron dissolved in the plating bath. By subjecting ten wires of the thus obtained copper-plated steel wires to co-winding test, the adhesive property of the plated layer was determined based on the number of the wires with no peeling in the copper plated layer.

Additionally, electrolytic pickling and electroplating were performed in the same manner as described above, except that thiourea was not added in the electrolytic pickling solution. The adhesive property and the amount of dissolved iron (amount of dissolved iron per unit surface area of the plated material) were measured. Table 1 shows the results.

Table 1

Thiourea	Adhesive property	Dissolved iron (g/m^2)	Remarks
Added	10/10	0.5	Example
Not added	6/10	1.7	Comparative Example

As is evident from Table 1, in the case of the method according to the present invention (Example), the amount of iron dissolved in the plating bath was extremely small and there was no case in which the adhesive property of the plated layer was defective. On the other hand, in the case of Comparative Example in which thiourea was not added, the amount of iron dissolved in the plating bath was large; displacement plating reaction occurred; and as much as 40 percent of the plated layer had a defect in terms of the adhesive property.

Example 2

Electrolytic pickling and electroplating were performed in the same manner as in Example 1 while using different kinds of displacement plating inhibitors, and the adhesive property of the copper plating and the amount of iron dissolved in the electroplating bath were examined. For reference, the effect obtained when the displacement plating inhibitor was added in the electroplating bath was examined.

Table 2 shows all the results.

Table 2

Displacement plating inhibitor			Adhesive property	Dissolved Iron (g/m^2)	Remarks
Addition target	Kinds	Addition amount			
Electrolytic pickling solution	Thiourea	0.1 g/l	10/10	0.5	Example
	Allylthiourea	0.1 g/l	10/10	0.8	
	Acetylthiourea	0.1 g/l	10/10	0.4	
	Amine A	1 cc/l	0/10	1.1	Comparative Examples
	Amine B	1 cc/l	0/10	1.1	
	Amine C	1 cc/l	0/10	1.0	
Electroplating solution	Thiourea	0.1 g/l	7/10	0.7	Reference Examples
	Allylthiourea	0.1 g/l	7/10	0.6	
	Acetylthiourea	0.1 g/l	7/10	1.0	
	Amine A	1 cc/l	0/10	1.4	
	Amine B	1 cc/l	0/10	1.8	
	Amine C	1 cc/l	0/10	1.8	
No addition			6/10	1.7	

Amine A: Ibit No. 8-600 (Product name, Sumitomo Chemical Co., Ltd.)

Amine B: Ibit No. 600-LA (Product name, Sumitomo Chemical Co., Ltd.)

Amine C: Ibit No5808-600 (Product name, Sumitomo Chemical Co., Ltd.)

As is evident from Table 2, although assumably the amine compounds were positively charged in the electrolytic pickling solution, there was no sign of the adhesive property-improving effects and further the adhesive properties were far inferior to that in the case where none of the agents was added. Moreover, thiourea or a similar compound showed excellent adhesive property-improving effects only when it was added in the electrolytic pickling agent, and thus a sufficient effect could not be obtained when it is added only in the electroplating solution.

Example 3

Thiourea, allylthiourea, and acetylthiourea were

selected as the displacement plating inhibitor, and the relations between each of the addition amounts and the adhesive property were examined according to the method described in Example 1.

Fig. 1 (for thiourea), Fig. 2 (for allylthiourea) and Fig. 3 (for acetylthiourea) show the results.

As is evident from Figs. 1 to 3, in order to achieve sufficient adhesive property, it is necessary to add thiourea in an amount of not less than 0.08 g/l, or allylthiourea in an amount of not less than 0.01 g/l, or acetylthiourea in an amount of not less than 0.02 g/l in the electrolytic pickling solution.

Example 4

Copper plating was performed in the same manner as in Example 1, except that 0.1 g/l of thiourea was added in the pickling solution and a simple immersion-pickling method was employed without power distribution. The adhesive property of the resulting copper-plated steel wire was 8/10, which indicates that the resulting product has a 20% chance of having the adhesive defect.

Namely, even if a considerable amount of thiourea is added in the pickling solution, the goal of the present invention cannot be achieved unless the electrolytic pickling method is employed.

4. BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 to 3 each illustrates a graph showing relations between the adhesive property and the addition amount of thiourea, allylthiourea or acetylthiourea.

Applicant: KOBE STEEL LTD.
Agent: Patent Attorney, Kazuhisa UEKI

Fig. 1

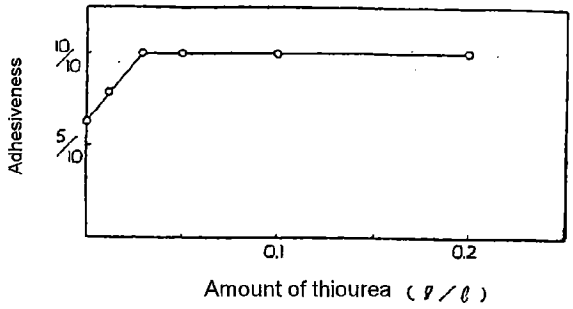


Fig. 2

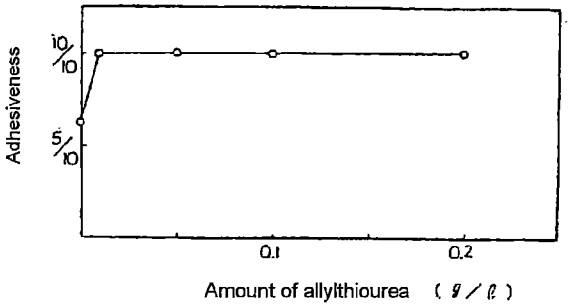


Fig. 3